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Arthur D. Little, Inc.
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ENVIRONMENTAL ASSESSMENT MEASUREMENT METHODS FOR ORGANIC SPECIES

By

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16. ABSTRACT The report summarizes work by the contractor on sampling and analysis methods for organic species relating to environmental assessment and control technology. The term-level-of -effort work involved assignments carried out under separate technical directives (or tasks). Most of the work has been published in detailed technical reports for each directive. This report summaries the studies and alerts readers to the availability of the technical reports.

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FOREWARD

This report summarizes the work which was carried out by Arthur D. Little, Inc., on a program entitled "Sampling and Analysis Methods for Organic Species as Related to Environmental Assessment and Control Technology Programs." The work was carried out over a three year period from March 1976 to March 1979 under EPA Contract No. 68-02-2150. The contract was a term-level-of-effort type and each assignment was carried out under a separate technical directive.

The majority of the work carried out under this contract has been published in detailed technical reports for each directive. The purpose of this report is to summarize the studies which were carried out and to alert interested readers to the availability of specific reports.

This work was carried out for the Process Measurements Branch (PMB) of the Industrial Environmental Research Laboratory at Research Triangle Park under the direction of Dr. Larry D. Johnson, Project Officer, whose encouragement and guidance throughout the program is gratefully acknowledged. The active participation of the PMB branch chief, Mr. James Dorsey, during the course of the program was most welcome and is also gratefully acknowledged. The program manager at Arthur D. Little, Inc., was Dr. Philip L. Levins. Many staff members at Arthur D. Little contributed to the individual assignments and assumed full responsibility for many of them. Their dedication and efforts contributed in large measure to the success of the program and are gratefully acknowledged. The individual contributors, while too many to list here, are indicated for each technical report.

I. Introduction

The Environmental Protection Agency has on-going studies related to environmental assessment and control technology development projects for the stationary source energy and industrial process programs. The Process Measurements Branch of the Industrial Environmental Research Laboratory at Research Triangle Park has provided support to those studies through a series of contracts whose focus was organic and inorganic measurement techniques, particulate sampling and characterization, fugitive emissions measurement methodology and quality assurance programs. The work described in this report dealt with evaluating and developing new techniques for the sampling and analysis of organic species.

The studies carried out in the course of the program were grouped into several major categories which included:

- Evaluation and development of measurement methods.
- Preparation of guideline and procedures manuals.
- Sampling and analysis support to on-going programs.
- Adaptation of existing methods for particular programs and evaluation of the applicability of certain methods.
- Review of measurement and test programs.

As part of this program a continuing review of new technology was carried out, in order to be able to apply new concepts and techniques to the measurement programs on a timely basis. As new methods surfaced, they were reviewed with the Project Officer to determine whether specific studies should be carried out to assess the applicability of the technique to the EPA program needs.

The studies carried out under the program can be categorized into three program areas:

- Research and Development
- Sampling and Analysis Program Support
- Technical Assistance

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The research and development tasks generally involved the development or evaluation of new methodology for environmental assessment and control technology measurements. Support was provided to various EPA programs in tasks ranging from analysis of supplied samples to assistance in source sampling and the preparation of manuals. Quick response technical assistance was available through the program to a wide range of people in EPA, contractor laboratories and industry.

Detailed technical reports were provided for each of the major tasks which have been completed under this contract; these are available either from the EPA or NTIS. A list of reports produced under this contract is given in Section V. Completed directives which were issued under the contract are as follows:

Research and Development

Technical Directive	Description
10102	A multi-task directive to evaluate various aspects of the Level 1 organic sampling and analysis procedures.
10202	Development of specific Level 2 procedures for a variety of organic groups, especially polychlorinated biphenyls (PCB) and polynuclear aromatic hydrocarbons (POM).
10302	Evaluation and development of simplified (e.g., spot test) class analysis procedures.
10402	Investigation of the applicability of high resolution mass spectrometry (HRMS) methods to the analysis of complex samples.

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10501	Examination of storage and shipping effects on sample stability and contamination.
10601	Selection and characterization of adsorbents to be used in the sorbent trap module of the SASS and similar sampling systems.
10702	Evaluation of Level 2 procedures for the directed analysis of specific compound classes and investigation of reliable gas collection methods for qualitative analysis. Also, evaluation of Level 2 procedures for difficult to analyze samples.
10801	Development of a sorbent module procedure for the concentration of organic species from water for subsequent analysis.
10901	Development of the sorbent module portion of the FAST train; activities coordinated with TRC.

Program Support

20104	State-of-the-art literature review, carried on for the duration of the contract.
20202	Assist the Combustion Research Branch of IERL in the development of a Level 1 laboratory.
20402	Analyze PCB in fish in support of evaluation of a proposed PCB removal technology.

20502	Characterize the capabilities of the Level 1 organic analysis procedures in the context of the compounds associated with the multimedia environmental goals activities.
20602	Prepare a technical manual for the analysis of fuels.
20802	Participate in the textile industry pilot study evaluation of the Level 1 procedures.
20901	Determine the feasibility of sampling flares.
21202	Analyze samples collected by SASS trains using the Level 1 organic analysis procedures in conjunction with an evaluation of Level 1 procedures conducted by the Research Triangle Institute.
21301/ 21401	Development of approaches for sampling of atmospheric emissions from coal gasification.
21502	Analyze samples and prepare a final coordinated report for samples collected by Monsanto Research Corporation from a ferroalloy process in conjunction with a control technology evaluation.
21602	Analyze particulate samples from stoker furnace emissions for PAH.
21802	Evaluate organic analysis procedures used by EPA Effluent Guidelines Division contractors for analysis of aqueous effluent samples from the organics and plastics industry.

Several other directives were issued under the contract and later either deferred for future study or merged with other directives for reporting purposes.

The activities carried out under these directives are summarized briefly in the following sections. For full details of the results derived from a particular directive the reader is referred to the reports developed in connection with that effort.

The results of some tasks were simple letter reports or technical sections that were incorporated into the reports of other contractors. Details of these activities can be obtained from the Project Officer or the author.

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II. Research and Development Studies

A. Evaluation of Level 1 Sampling and Analysis Procedures

The overall objective of the work carried out under this directive was to evaluate the Level 1 organic sampling and analysis procedures as proposed in the June, 1976 Level 1 Procedures manual (IERL-RTP Procedures Manual: Level 1 Environmental Assessment. Report EPA-600/2-76-160a, June 1976). Priorities of this study included: development of a resource of information concerning the behavior of compounds and classes of compounds when subjected to Level 1 procedures and identification of problems and limitations of the proposed procedures that might require revision in methodology. The question of stability of Level 1 samples collected for organic analysis was addressed in other studies for which separate reports have been issued.

The Level 1 organic analysis methodology is designed to identify the major classes of organic compounds present in a process or effluent stream and to estimate the concentrations. The overall organic procedures as originally proposed are summarized in Figure 1 (sampling) and Figure 2 (analysis).

The report prepared for this task presents the results of a series of experimental studies of the organic analysis procedures as proposed and as eventually modified. Laboratory studies are described here in discrete independent chapters that deal with the individual experimental investigations. The topics are presented in an order that seems to be logical in retrospect. The experimental work was carried out at Arthur D. Little, Inc. over the period January, 1977 to December, 1978 and documented in monthly progress reports.

This report also includes several examples of Level 1 organic analysis data for samples analyzed according to the revised procedures. The results for a coal sample and a fuel oil sample and a SASS train sample of an actual emission source are presented in the Level 1 report format.

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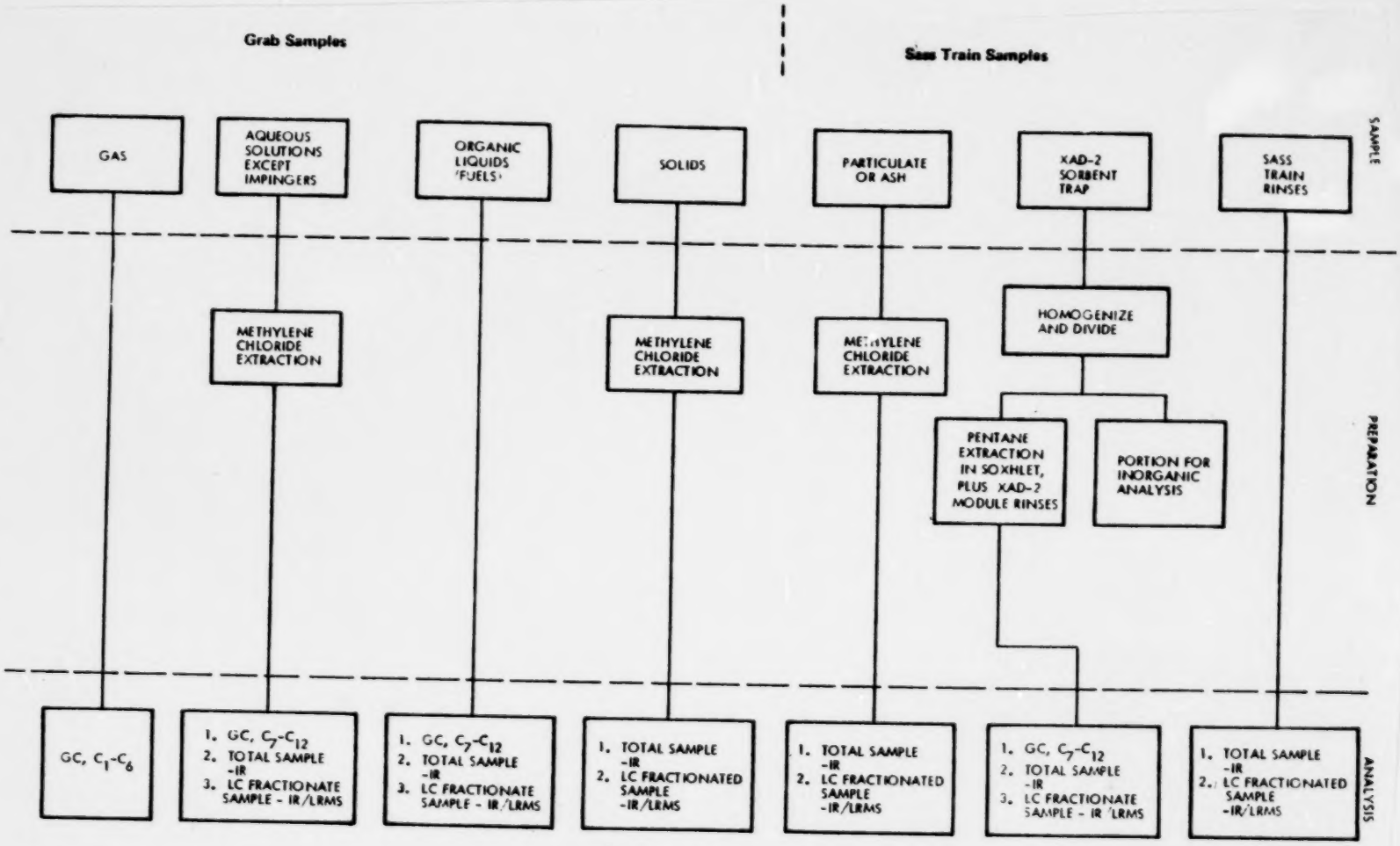

FIGURE 1 ORIGINAL MULTIMEDIA OVERVIEW OF SAMPLES FOR ORGANIC ANALYSIS

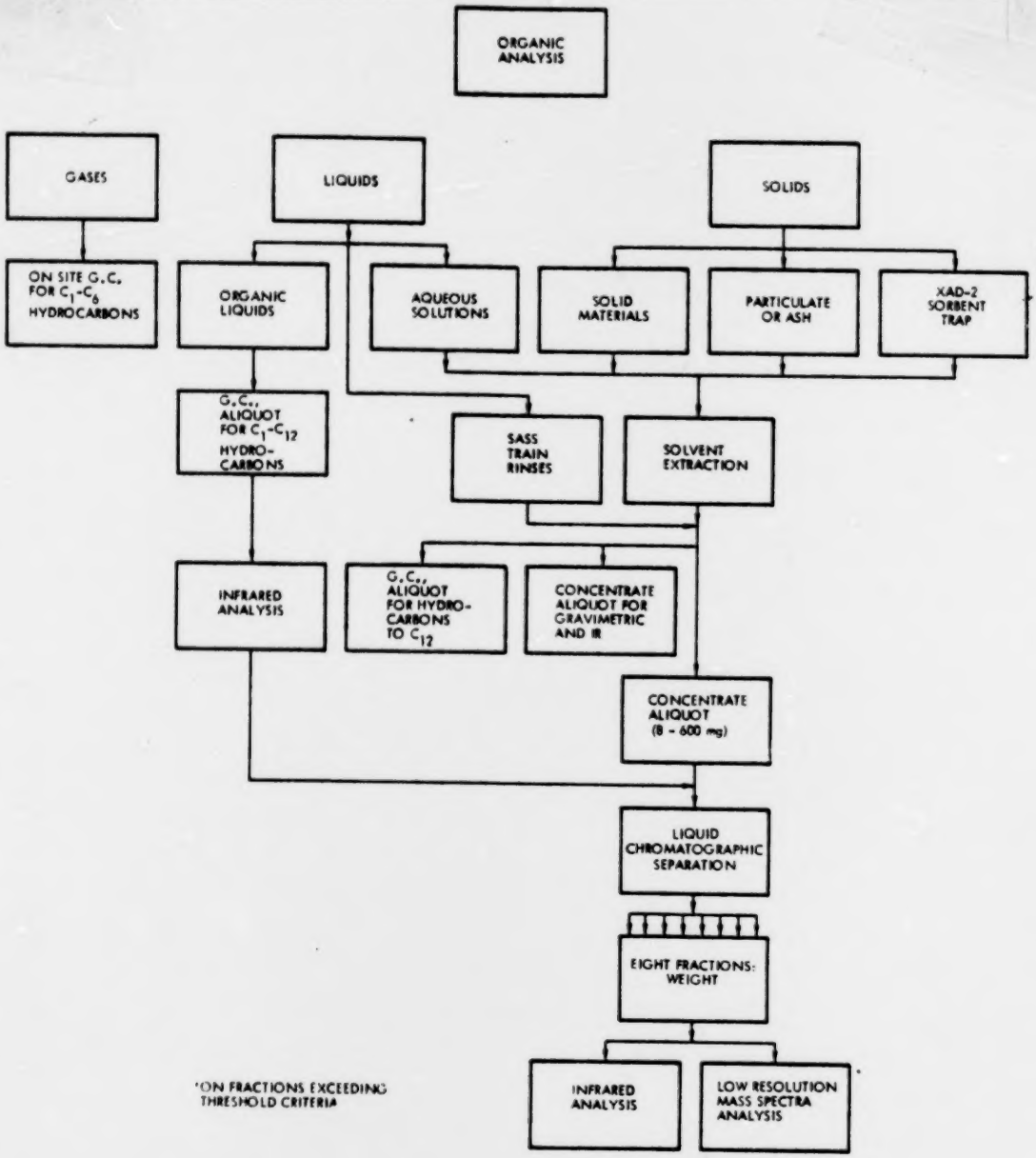

FIGURE 2 ORIGINAL LEVEL 1 ORGANIC ANALYSIS FLOW SCHEME

Major sections of the report summarizing the Level 1 activities are:

FIELD GC ANALYSIS OF ORGANIC GASES

PREPARATION AND CHARACTERIZATION OF XAD-2 RESIN

EXTRACTION OF AQUEOUS SAMPLES

EXTRACTION OF SLUDGE/SLURRY SAMPLES

ANALYSIS OF VOLATILE SPECIES IN ORGANIC EXTRACTS:
TCO AND SOLVENT EXCHANGE

ELUTION PATTERNS IN LEVEL 1 LC

RUGGEDIZATION OF LEVEL 1 LC PROCEDURE

REPORT FORMATS FOR LEVEL 1 ORGANIC ANALYSIS RESULTS

EXAMPLE OF APPLICATION OF LEVEL 1 PROCEDURES TO FUEL SAMPLES

EXAMPLE OF APPLICATION OF LEVEL 1 PROCEDURES TO A SASS TRAIN SAMPLE

APPENDIX A: REVISED LEVEL 1 ORGANIC ANALYSIS TECHNIQUES

APPENDIX B: PREPARATION OF XAD-2 SORBENT RESIN

The feasibility of incorporating an electronic sensor into the sorbent module of the SASS train for the purpose of detecting breakthrough of substances normally sorbed in that module was also investigated as part of the activity under this directive. Desirable performance characteristics of such a device were proposed, and a number of types of detectors were considered in terms of those characteristics. Although no existing detection systems were judged to be entirely satisfactory, the one that appeared to most nearly meet the requirements was the Metal Oxide Gas Sensor (MOGS). The applicability of this type of device was evaluated in part by extension of demonstrated properties of the detector in detection of small quantities of various organic vapors in air at room temperature, and partly by limited laboratory experiments.

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B. Revised Level 1 Organic Analysis Procedures

A revised Level 1 Organic Analysis procedures chapter was prepared for inclusion by Research Triangle Institute in the final version of the Level 1 sampling and analysis procedures manual.

The overall organic Level 1 analysis scheme for prepared samples is shown in Figure 3. The data expected to be generated for each type of Level 1 sample is indicated in Table 1. A significant contribution to the effort under this task was the development of a systematic reporting methodology which would summarize the detailed chemical analysis data in a form more readily utilized by those evaluating the data. An example of a summary report using the new format is given in Table 2. A key feature of the report format is that the individual chemical analysis data on each component or LC fraction are summarized by major chemical groups for the total sample.

C. Development of Level 2 Analysis Procedures

The objective of this directive was to evaluate the potential for methods such as HPLC, GC, GC/MS, HRMS, etc., to provide the basis for developing specific test procedures for groups of compounds like PCBs, POM, nitrosamines, etc. Review of the literature indicated the potential for the development of reliable methods for PCBs and POM and procedures were developed and validated for these groups using GC/MS techniques.

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For the PCB method, three areas of effort were defined. 1) Pertinent publications were reviewed to allow drafting of a tentative PCB analysis procedure. 2) Laboratory experiments were conducted to test the tentative procedure using well characterized reference materials 3) Verification of the PCB analysis procedure was made using complex organic samples, representative of the types of samples expected in environmental assessment studies.

The method utilized describes a GC/MS procedure that overcomes problems encountered when using GC procedures (previously used to determine PCBs

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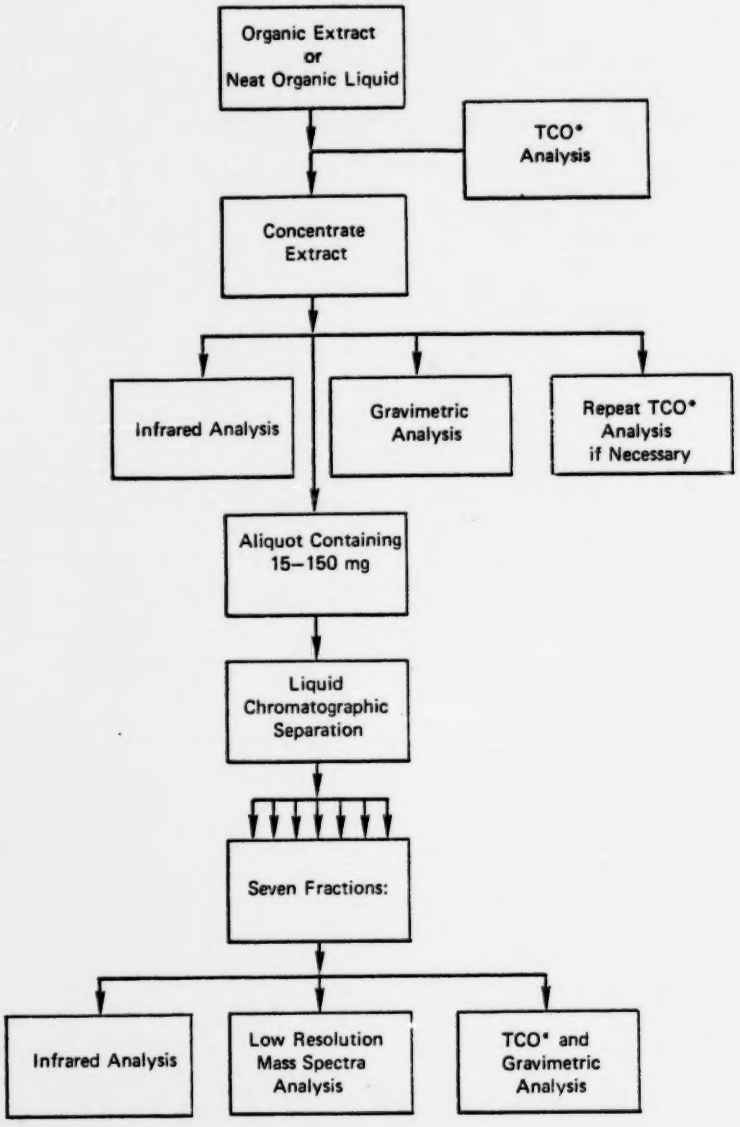

*TCO analyses are not necessary for samples for which process or collection temperatures were 200°C (400°F) or higher.

FIGURE 3 REVISED ORGANIC ANALYSIS METHODOLOGY

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TABLE 1

SUMMARY OF EXPECTED DATA FROM REVISED LEVEL 1 ORGANIC ANALYSIS

SAMPLE	On-Site GC	TCO	GRAV	IR	LC*
Gases - Grab Sample	✓				
SASS					
>10 μm particulate			✓	✓	✓
3-10 μm particulate			✓	✓	✓
1-3 μm particulate			✓	✓	✓
<1 μm particulate			✓	✓	✓
Rinse of particulate modules			✓	✓	✓
XAD-2 Resin combined with rinse of sorbent module		✓	✓	✓	✓
Sorbent Module Condensate		✓	✓	✓	✓
SOLIDS					
Flyash; Clinker			✓	✓	✓
Organic Feed Stock		✓	✓	✓	✓
Coal		✓	✓	✓	✓
LIQUIDS					
Effluent Water		✓	✓	✓	✓
Organic Feed Stock		✓	✓	✓	✓
Fuels		✓	✓	✓	✓

*Includes GRAV + IR on all fractions; TCO and LRMS when sample quantity is sufficient.

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TABLE 2

SUMMARY OF RESULTS FOR ORGANIC EXTRACTS FOR SASS TRAIN SAMPLES

$\sum$, mg/m^3

	Particulate Module		Sorbent Module			TOTAL
	Rinses*	>3 μm	<3 μm	Resin	Rinse	Condensate†	
CATEGORIES							
Aliphatic Hydrocarbons		<0.06	<0.04	0.3	0.8		1.1
Aromatic HC's - benzenes				0.6			0.6
Fused Aromatics, MW <216		0.25	0.15	6.3	22		29.
Fused Aromatics, MW >216		0.25	0.15	4.2	21		26.
Heterocyclic N		0.31	0.19	0.6	19		20.
Heterocyclic S		<0.06	<0.04	0.4	2		2.4
Heterocyclic O		<0.06	<0.04	0.2	2		2.2
Phenols		0.06	0.04	0.1			0.2
Esters		0.18	0.11	0.1	0.1		0.5
Carboxylic acids		<0.06	<0.04	0.3	0.3		0.6
Sulfur					0.2		0.2
Inorganics				0.1			0.1
Unclassified		0.06	<0.04	0.2			0.3
Silicones		0.06	0.04				0.1

* Rinses corresponded to 0.03 mg/m^3 of organics and were not subjected to LC-IR-LRMS analysis.

† No condensate was collected for this sample.

in solids and water) on emissions from combustion sources. The GC/MS procedure, which relies on selected mass scanning in restricted regions of the chromatograms, was developed because in the combustion process the distribution pattern of the individual PCBs changes, rendering invalid the pattern matching approach used with the gas chromtographic/electron capture detection (GC/ECD) method.

Three GC/MS methods were evaluated for the measurement of specific POM compounds. The use of liquid crystal chromatographic phases was recommended for the measurement of a few specific POMs, e.g., benzo(a)-pyrene. GC/MS methods for a wide range of POMs were studied for both capillary and packed GC columns. The three methods for specific POM identifications were verified with collected environmental samples of different kinds.

EPA reports were published describing the details of the methods developed for each of these groups of compounds. The PCB work was also published in the American Institute of Chemical Engineers Journal, following presentation at one of their meetings.

D. Development of Simple Specific Compound Class Analysis Procedures

The purpose of this directive was to determine whether techniques existed which might lead to the development of simplified spot test type of procedures for specific classes of compounds. A review of the literature and previous Arthur D. Little, Inc. research indicated that a spot test procedure might be feasible for PAH.

A fluorescent spot test was devised for polycyclic aromatic hydrocarbons (PAH) based on the sensitization of the inherent fluorescence of such compounds. The basic procedure involves spotting a filter paper with a small amount of the sample solution, adding naphthalene, in solution, to the spot and visually observing the fluoresence under illumination with a simple ultraviolet light source. On filter paper 10 pg of PAH in a spot of 0.25 cm diameter can generally be visualized when treated with naphthalene. In the case of benzo(a)pyrene, 1 pg has been detected.

An EPA report was published describing this work. The work was presented at a Battelle Polynuclear Aromatic Hydrocarbons symposium and published in the proceedings.

E. Environmental Applications of High Resolution Mass Spectrometry

Development of survey analysis procedures for organic species in environmental samples is a demanding challenge. The nature of a survey request implicitly requires that the effort, and therefore cost, applied to a survey analysis be minimized. Yet the nature of the information required to assess potential hazards associated with a stream requires chemical structure information for the organic species present in the stream to be as specific as possible.

High resolution mass spectrometry (HRMS) has the inherent capability of providing exact chemical composition data for samples. The applicability of the HRMS method to complex environmental samples has been explored in this program. Two different approaches have been investigated. One involves generating the high resolution mass spectral information from a sample and then file searching, or matching, that information against a specified (fixed) list of compounds. The other approach involves the sorting of HRMS data into a simplified matrix from which the basic chemical character of a sample may be deduced.

The file-search method was explored with several samples using as a reference file, the list of about 2,000 chemicals prepared by the Research Triangle Institute for EPA/IERL. For the energy source samples studied, the match of precise masses observed with reference list chemicals was quite good. It is significant that achieving good matches required the use of the precise mass HRMS data; attempts at matching using only unit mass data were poor. This file-search approach may be useful for assessment studies within narrowly defined areas.

The alternative matrix approach was very successful in arranging the highly complex HRMS data in a form from which accurate chemical

composition data could be obtained. The value of the matrix technique has been demonstrated by the analysis of several environmental samples.

High resolution mass spectrometry is a very powerful tool for organic analysis and can make valuable contributions to survey and more detailed analyses.

A final report describing this research was submitted to EPA. The work was also presented at the Battelle Polynuclear Aromatic Hydrocarbon symposium and published in the proceedings.

F. Effects of Sample Storage and Shipping Conditions on Stability and Contamination

The purpose of the studies under this directive was to evaluate the effects of typical shipping and storage handling procedures on organic materials collected in Level 1 studies. Specific parameters reviewed included sample container composition (amber glass and high density linear polyethylene), head space composition (air or nitrogen), temperature (38°C, 21°C, 5°C), lighting condition (dark and diffuse sunlight) and catalytic species content. Three unique sample sets, representative of sample types obtained during a Level 1 environmental assessment, were formulated containing six model organic compounds. A three-week simulated shipping and storage cycle was used as representative of elapsed time between sample collection and analysis. All three experiments were designed in accordance with statistical principles appropriate for conducting factorial analysis. Experimental results were analyzed by the analysis of variance technique in order to assess the relative effect of each shipping/storage condition studied.

The major findings of the experiments were as follows:

- Generally, any reasonable combination of shipment temperature, head space composition, and storage condition can be utilized for the short-term storage of Level 1 survey analysis samples.

- These same conditions can be employed for the short term storage of samples undergoing quantitative chemical analysis where the accepted range of variation is ± 10 percent.

- Amber glass containers are preferred for sample storage over polyethylene bottles, as it has been found that spurious contaminants may be extracted from the container walls by contact with organic solvents.

- Diffuse sunlight can penetrate polyethylene containers and cause degradation in species that are photoreactive. Amber glass on the other hand will absorb the harmful wavelengths and prohibit photodegradation.

G. Gas Sample Storage Stability

One of several sub-tasks under a directive to evaluate Level 2 procedures was to determine the impact of sample container type on gas sample storage stability and contamination.

The suitability of several types of containers for the long-term storage of gas samples was compared in a laboratory study. The performances of glass bulbs and polymeric bags from two vendors were evaluated. A test gas mixture consisting of ethane, propylene, methyl chloride, methanol, ethylene oxide and benzene was prepared in order that the behavior of compounds of differing molecular weights and polarity could be studied. The test gas mixture was introduced into each of the three containers and the concentrations of the individual gaseous compounds were measured as a function of storage time, using gas chromatography.

The studies indicated that glass bulbs are the best overall choice, with no significant losses of the gases. Reactive and highly polar gases were preferentially lost in the polymeric sample bags. Relatively simple gases were stable in these sample bags. Contaminants were detected in the samples taken from the polymeric bags, presumably the result of

outgassing from the construction materials of the bags. These contaminants were found at very low ppb levels, but they could nevertheless interfere with trace analyses of collected gas samples. Therefore, the polymeric bags are recommended for the storage of relatively simple gases at high concentration levels, i.e., ppm or greater. The Calibrated Instrument's 5-layered bags were superior to the DuPont Tedlar® bags, with fewer interferences and less sample loss.

H. Selection and Characterization of Adsorbents for Use in the Sorbent Module of the SASS Train and Similar Sampling Systems

Previous work under EPA Contract No. 68-02-1332 (Report No. EPA-600/7-77-004, April 1977) had indicated the potential benefits to be gained in using the sorbent XAD-2 as the vapor collection component of sampling trains. The directive under this contract was designed to obtain a complete quantitative characterization of the XAD-2 and Tenax-GC sorbents and to study the influence of potential interferences on their collection efficiency.

Two chromatographic techniques, frontal and elution analysis, were applied to characterize sorbent cartridges packed with the Tenax-GC and XAD-2 sorbents.

Three diverse sorbate groups, consisting of eight distinct chemical classes, were studied as potential pollutants. Elution analysis of these vapors yielded specific retention volumes, V_g^T, which can be directly related to the breakthrough characteristics of the sorbent resins under a diversity of sampling conditions. Figure 4 shows the relationships observed between retention volume and boiling point for several compound groups. Adsorption coefficients, K_A, derivable from V_g^T, indicate the intrinsic affinity of the sorbent for each of the sorbate at challenge concentrations in the Henry's Law region.

Frontal analysis results confirmed the elution data for sorbate uptake of resins. A slight flow rate dependence for sorbate uptake was noted for XAD-2. Specific retention volume data extrapolated to ambient con-

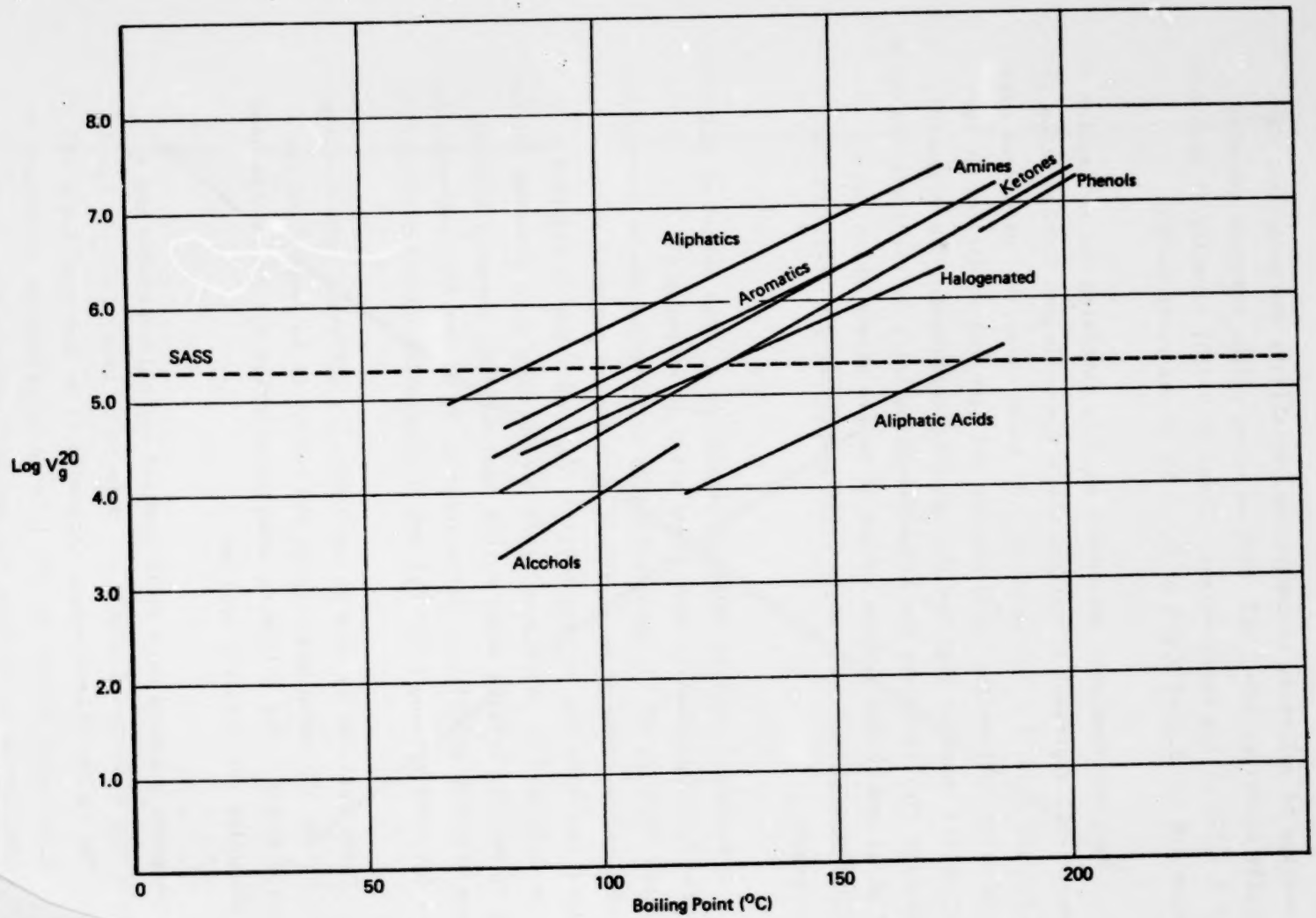

FIGURE 4 LOG V_g^{20} (mL/g) VS. BOILING POINT FOR INDIVIDUAL ADSORBATE GROUPS ON XAD-2

ditions correlated well with sorbate boiling point and molecular polarizability. These correlations allow breakthrough to be estimated for a variety of sorbate types.

The effects of combustion gases, carbon dioxide, water and the combined effect of carbon dioxide and water on the retention volume of trace level sorbates on XAD-2 and Tenax-GC were also studied during the program. The retention behavior of XAD-2 was relatively unaffected by the combustion gases studied. Introduction of water vapor led to V_g reductions of 0-4% for the non-polar sorbates studied and 13-17% for the two polar sorbates. Carbon dioxide at 10% (v/v) levels resulted in essentially no further decrease for XAD-2. On the other hand, the V_g values on Tenax-GC were reduced by 22-43% in the presence of water vapor, and an additional 25% decrease was observed when carbon dioxide was introduced.

Other sorbents have been investigated for collecting volatile and polar organics. The charcoals, Lot 104 (activated petroleum) and Lot 106 (activated coconut) and the Ambersorbs, XE-340 and XE-347, appear to be potential candidates for this purpose. The charcoals and Ambersorbs show V_g values three to five orders of magnitude higher than XAD-2 for non-polar sorbates. For alcohols, the differences are one to three orders of magnitude. The increased V_g's are only partially attributable to differences in surface area. Based on this study, the order of preference in selection of sorbents for collection of high volatile and polar organics, listed in order of decreasing intrinsic affinity (K_A), is: Charcoal Lot 104 > Ambersorb XE-340 > Charcoal Lot 106 > Ambersorb XE-347 > XAD-8 > Tenax-GC > XAD-2.

This work was published in two EPA reports.

I. Level 2 Sampling and Analysis Procedures

Level 2 sampling and analysis procedures have been recommended for samples collected in connection with environmental assessment studies. The pro-

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cedures are based upon the premise that the investigators are proceeding with a phased analysis approach.

Specific directed compound class analysis methods have been recommended for each major MEG category compound, where the Level 1 analysis has directed the analyst towards a particular group of compounds.

In cases where insufficient information would be available from the Level 1 studies, a more elaborate general scheme has been proposed for a Level 2 analysis, as shown in Figure 5. A key assumption in the proposed scheme is that whenever the Level 1 procedures were found to be inadquate for the sample characterization in the first phase of the study, the additional technqiues will be not only different but also more complex than those used in Level 1.

The level 2 organic sampling and analysis manual represents a step in the development of a general methodology for chemical and biological assessment of environmental effects of industrial effluents. It presents concepts and general guidelines, together with a number of more fully developed, tested, and validated Level 2 procedures. The accumulation of experience in sampling and chemical analysis of environmental pollutants is by no means complete, however. The process is expected to continue for some time, perhaps indefinitely. Users of the manual will therefore find a number of areas in which additional research and testing is needed, and in which present knowledge is insufficient to permit hard and fast procedures to be established.

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The Level 2 procedures manual has been published by EPA in an interim and final version.

J. Sorbent Module for the Extraction of Organic Species from Water

An attractive alternative to the use of solvents for collection of organics from large quantities of water is the use of an *in situ* continuous extractive sampler containing a solid sorbent material. One of the earlier devices of this type, once widely used in the field, was the EPA's carbon

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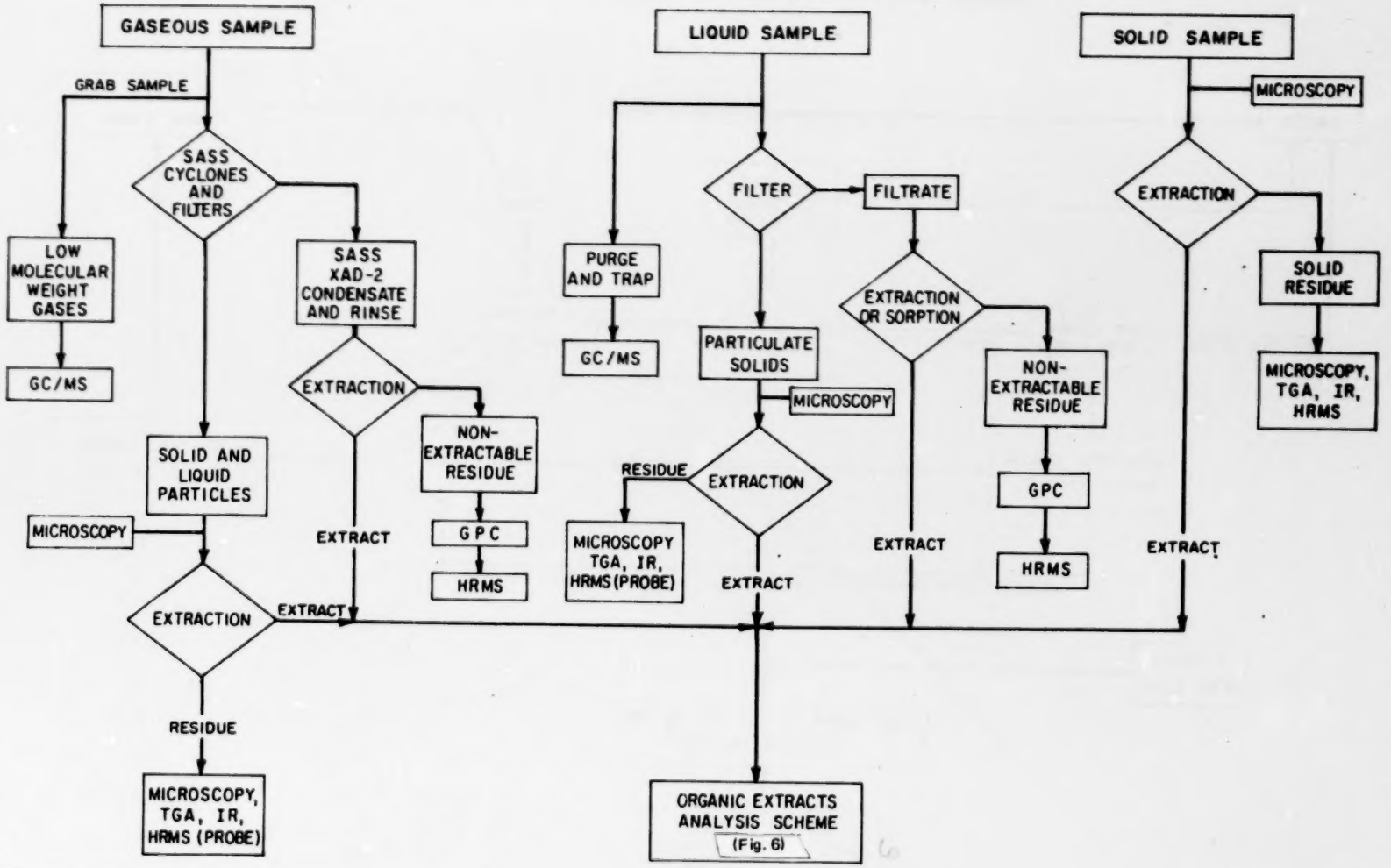

FIGURE 5 LEVEL 2 ORGANIC ANALYSIS SCHEME

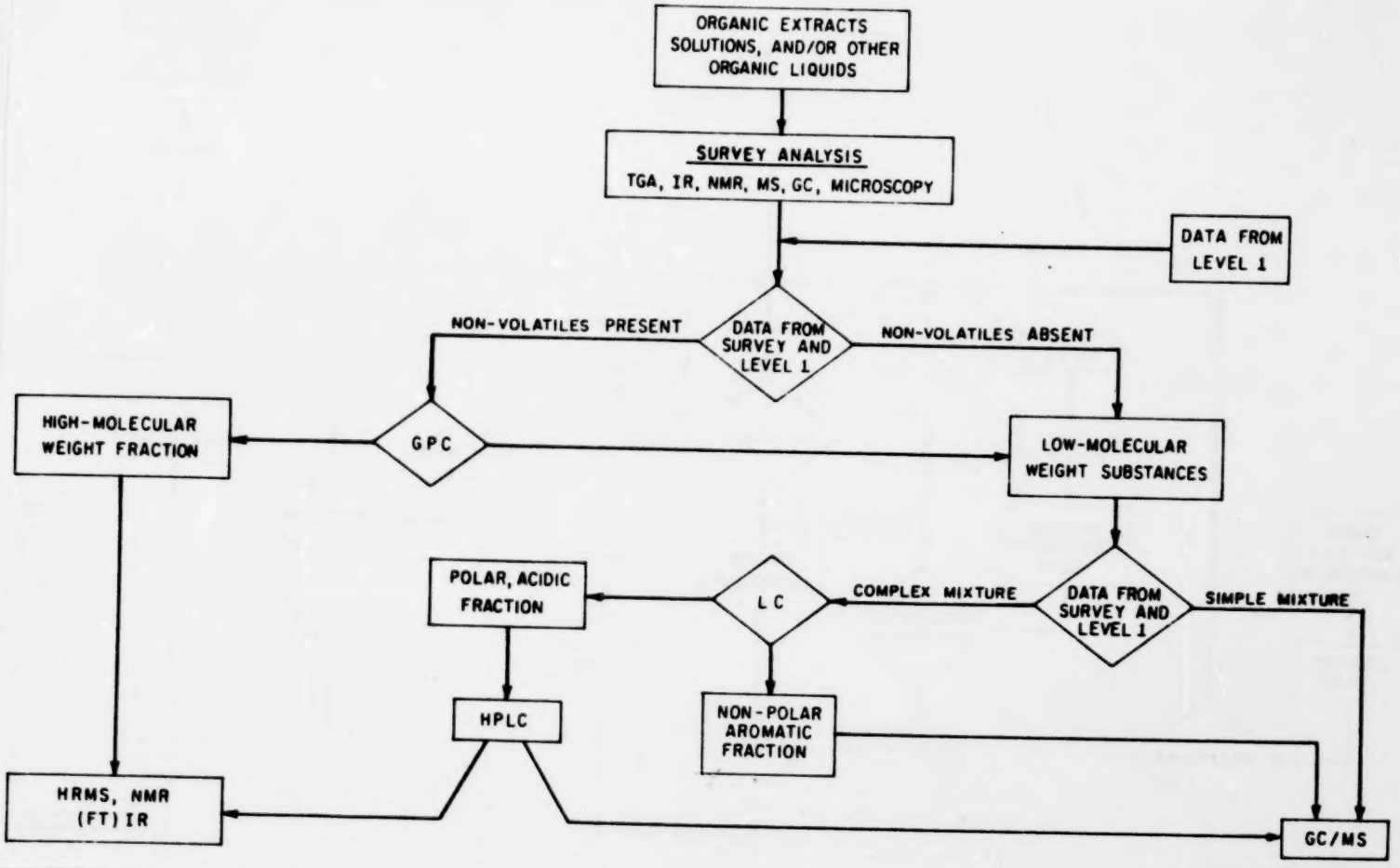

FIGURE 6 ORGANIC EXTRACTS ANALYSIS SCHEME

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adsorption module (CAM) with generally good collection efficiency, but low recoveries, for organics. A number of previous workers have done laboratory studies on the use of macroporous resins and have determined overall recoveries of selected organic compounds from water, under conditions designed to simulate sampling applications.

The work under this contract involved a systematic laboratory investigation of the applicability of macroreticular resins for general and compound specific sampling of organics, based on small scale, chromatographic experiments.

The basic approach used in this work was the generation and analysis of the frontal breakthrough curve produced by challenging a sorbent cartridge with an aqueous solution of organic analyte at constant flow rate. A number of sorbents were studied including XAD-2, XAD-7, IRA-904, IRA-93 and XE-347.

The studies demonstrated that:

1. XAD-2 is an effective resin for sampling non-polar and moderately polar organics; it is not effective for very polar species.

2. The linear velocity of water passed through an XAD-2 bed should be be very low for efficient collection of moderately polar organics. PAH collection is not especially sensitive to flow rate.

3. Of the macroreticular resins tested, as possible back-ups to an XAD-2 sampler, the carbonaceous XE-300 series appears most promising for very polar species.

4. The chromatographic approach used in this work allows rapid, simple quantitative evaluation of resins for sampling applications. The results can be extrapolated to larger scale systems.

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This work was presented at the third Polynuclear Aromatic Hydrocarbon symposium and published in the proceedings.

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III. Program Support Activities

A. Combustion Research Branch Laboratory Level 1 Analysis Manual

The Combustion Research Branch IERL/RTP, established a program to apply the Level 1 Environmental Assessment (EA) procedures to the combustion sources used in its in-house programs. A laboratory manual was specifically written to describe the application of Level 1 analytical procedures to the CRB objectives. The manual is intended for use by analytical chemists in the in-house laboratory program. It is intended to supply information which will bridge the gap between the "IERL-RTP Procedures Manual" and the detailed step-by-step compilations of procedures provided by published (EPA, ASTM, AOAC, etc.) methods or by instrument manuals which are provided by manufacturers of individual analytical instruments.

The manual assumes that the reader is an analytical chemist who is familiar with normal laboratory operations and manipulations. It is not intended for use by inexperienced professional staff or technicians. Procedures for sample handling and analysis are spelled out in detail whenever they are especially critical, unusual, or unique to the Level 1 environmental assessment procedures.

In this manual, there is a brief discussion of some factors which contribute critically to overall analytical quality control (Section II). Section III presents the overall analytical plan for the CRB Level 1 Environmental Assessments with a description of the facilities tested, types of samples to be taken and analyses to be performed. Section IV contains procedures for performing the various sample preparation steps required. Finally, Section V describes the particular analytical procedures required.

Instrumentation and staffing requirements were also prepared as a separate report.

The work was carried out as part of an effort coordinated with the Aerotherm Division of Acurex Corporation who supplied the detailed sampling requirements.

This work was described in reports submitted to EPA.

B. Measurement of PCB in Sheepshead Minnows

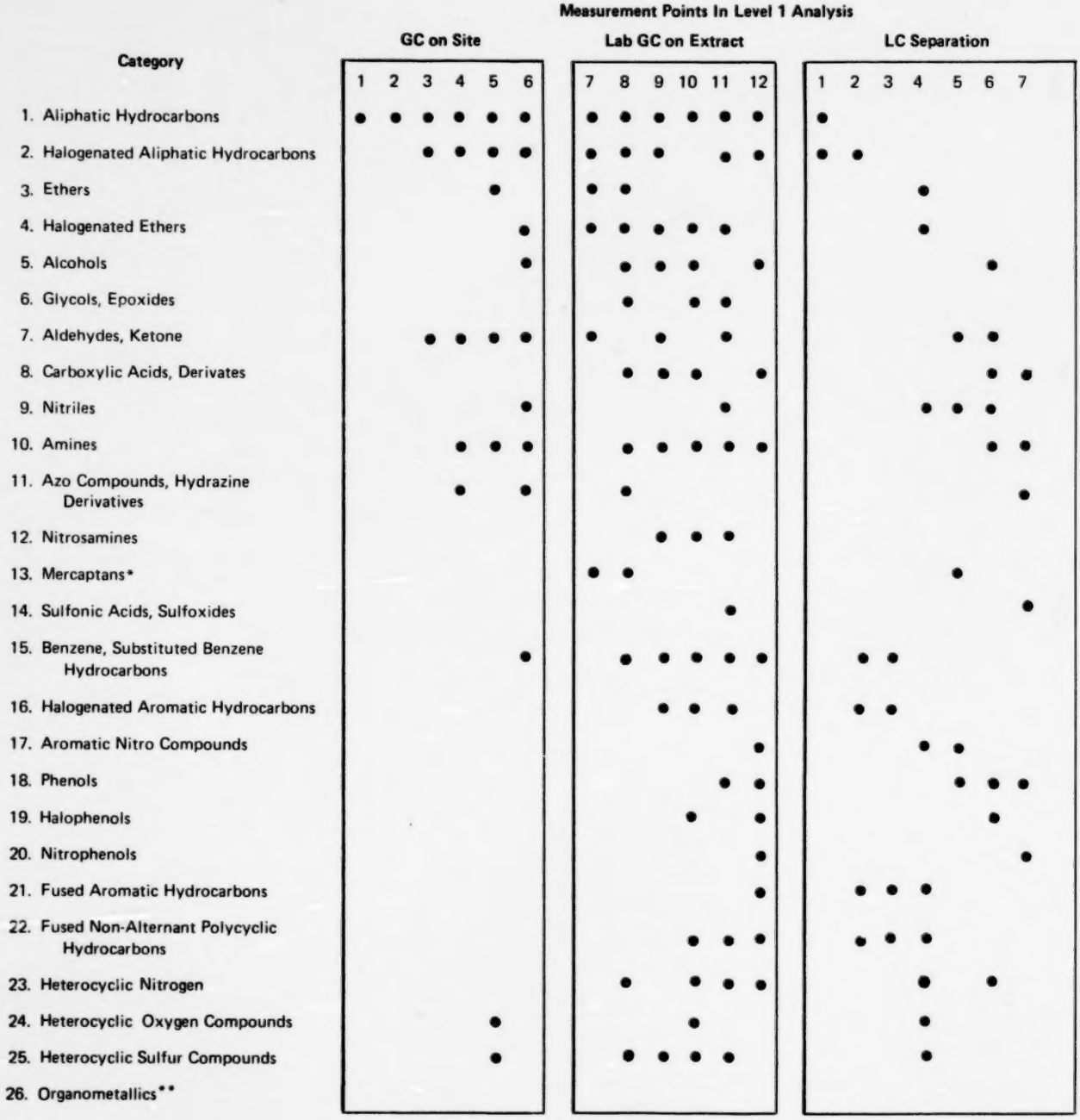
This directive was initiated to support EPA-sponsored research studies on the efficacy of the reductive degradation column developed by Envirogenics Systems Company (9255 Telstar Ave., El Monte, California 91731) for the removal of polychlorinated biphenyls (PCBs) from water. The column packing was made with a specially prepared catalyst of iron and copper, mixed with sand and marble chips. This column was tested using an approach which involved three independent facilities--Bionomics (Gulf Breeze Highway, Pennsacola, Florida 32507), Envirogenics, and Arthur D. Little, Inc. Bionomics controlled the experimental runs for the bioaccumulation tests using sheepshead minnows (Cyprinodon variegatus) as the indicator species; Envirogenics analyzed the relevant water samples; and Arthur D. Little, Inc., carried out the analyses of the corresponding samples of sheepshead minnows. Aroclor 1016 was used as the representative PCB for all phases of this joint study. The report covers only the activities related to the analyses of fish samples for PCB in accordance with the EPA procedure using GC/ECD analysis. The report has been supplied to EPA.

C. Characterization of the Level 1 Procedures in the Context of The Multi Media Environmental Goals Program

The IERL-RTP has developed a multi media environmental goals (MEG) program to be used in environmental assessment studies of energy processes. A theoretical evaluation was carried out to determine whether the Level 1 analysis methods would be capable of identifying each of the organic compounds in the MEG list. A summary of that evaluation shown in Table 3 indicates that the Level 1 scheme should be capable of detecting all of the MEG compounds if they are present in a source emission.

TABLE 3

SUMMARY OF LEVEL 1 ANALYSIS SCHEME AND MEG ORGANIC COMPOUNDS



*Reactive Sulfur Species Analyzed on Special Field GC/FPD

**Too General for This Evaluation

D. Technical Manual for the Analysis of Fuels

In support of IERL-RTP Combustion Research Branch, a manual was prepared for use as a guide in research projects concerned with fuel combustion. Basically, it describes and discusses standard methods of sampling and analysis for a variety of hydrocarbon fuels. The analyses covered are those of prime concern to the combustion engineer; no attempt is made to cover all analyses that may be required in a complete Environmental Assessment of any fuel combustion process. For each fuel covered, the manual indicates the analyses that are likely to be required, the preferred method of analyses, and available sampling procedures. For each method of analysis listed (preferred plus alternates, in many cases), the manual summarizes the method, discusses its applicability, and describes its precision. The manual covers gaseous fuels, liquid petroleum fuels, waste lubricating oil, shale oil, coal liquids, methyl fuel, coal, coke, refuse-derived solid fuels, and peat. The appendices give: the availability of Standard Reference Materials for fuel-related analyses; laboratory directories; typical values (or ranges) of parameters specified for each fuel; and results of fuel analyses conducted by the contractor.

The manual was published as an EPA report.

E. Support to Level 1 Environmental Assessment Study

The task performed under this Technical Directive was designed to provide technical assistance, guidance and observation in support of an extended operational test of the Level 1 sampling and chemical analysis procedures for Environmental Assessment (EA). The actual sampling and analysis work was done by an EA contractor, Monsanto Research Corp. (MRC), Dayton, Ohio, and was performed in conjunction with sampling and analysis work that was required for a related source assessment study for "priority pollutants." The effluent streams sampled were all aqueous liquids discharged from secondary treatment facilities associated with fifteen textile manufacturing and processing plants located at various points in the continental United States.

Because of difficulties encountered in scheduling of visits under strict time deadlines, only one visit was made by the Level 1 monitoring contractor (ADL) to a sampling site. One visit was made subsequently to the EA contractor's laboratory to observe analytical methods and to discuss problems and early results at a time when part of the work had been completed, and one visit was made by one MRC staff member to the Arthur D. Little, Inc. laboratory. Telephone calls and letters were used as the principle means of discussing day-to-day problems.

A limited amount of experimental work was conducted in order to find solutions to problems that were encountered by the EA contractor. Suggestions for a data-reporting format were offered, some of which were incorporated into the EA's final report. Review of the final report was undertaken for the purpose of discovering opportunities for improvement of the reporting format, and to identify any remaining problems in the sampling and analysis protocol.

F. Ferroalloy Process Emissions Measurement

Sampling and analysis were undertaken to characterize and quantify particulate, organic and inorganic chemical emissions in effluents from a totally sealed metallurgical furnace at a ferroalloy production facility. Effluents were sampled by Monsanto Research Corporation downstream of a Venturi scrubber during silicomanganese production (Test I) and upstream of the scrubber during ferromanganese production (Test II). Sampling and analysis methodology used was essentially that of EPA's Level 1 Environmental Assessment procedure, supplemented by a specific analysis of polynuclear aromatic hydrocarbons. Analysis of the samples was carried out in the Arthur D. Little, Inc., laboratories.

Measurements made in Test II indicated a particulate loading of 68,000 mg/m^3, equivalent to 17 Kg/MW-hr. Very high levels of organics, including high molecular weight aromatic hydrocarbons, were found. Compound categories found include some polynuclear aromatic species recognized as carcinogens. High levels of arsenic were also measured in Test II.

Measurement of gaseous effluent from the Venturi scrubber in Test I indicated much lower levels of all species of concern. Particulate loading was estimated to be 64 mg/m^3, equivalent to 0.016 Kg/MW-hr. The major organic compound categories were simple aromatic hydrocarbons and low molecular weight polycyclics. The arsenic level was estimated to be less than 0.5 mg/m^3.

In these tests, good agreement was observed between the results of Level 1 orgnaic analysis and the specific analysis of polynuclear aromatic hydrocarbons. Good agreement was also found between the atomic absorption and spark source mass spectroscopic analyses of arsenic and antimony.

Because the two tests corresponded to different ferroalloy production processes, the results cannot provide a quantitative measure of the Venturi scrubber efficiency. However, the data imply good particulate removal efficiency. The Venturi scrubber also appears to be effective for removal of polynuclear aromatics, especially species in the higher molecular weight range that includes the recognized carcinogenic POM.

The EPA published report resulting from this work provides an excellent example of the proper use of the Level 1 analysis scheme and reporting format.

G. Flare Sampling Feasibility Study

Approaches were evaluated for collection of a sufficient quantity of samples from flares to enable an adequate analysis for an Environmental Assessment.

Despite the recent advances in the design and operation of flare systems, few factual data exist which describe the combustion efficiency of the process. Unlike other combustion effluents, which have been extensively reviewed, the emissions from flare systems have not been characterized because no methodology has yet been identified that is

capable of acquiring the necessary data. Although sufficient analytical expertise exists to enable researchers to characterize the probable chemical components of flare system emissions, no appropriate extractive, in situ or remote sensing technique has been found that is suitable for sample collection or observation. Therefore, the purpose of the task was to review the available information describing flare system design and operation, and then to determine whether any method of sample collection or observation could be applied to obtain data which would be useful in environmental assessment studies.

Flares are basically emergency combustion systems whose operation is, by design, irregular. Flares are generally large and would have a safe personnel approach distance of several hundred feet when operating, due to the thermal radiation flux.

Only two methods of extractive testing appear to be possible for the Level 1 assessments of emissions originating from flare stacks. The first system considered involves the reproduction of the flare stack on a smaller scale. The flow through the simulated unit would be two or three orders of magnitude less, but the design would attempt to duplicate all combustion properties of the larger unit. A SASS train would be used to sample the emissions from the smaller unit.

The second system involves flying through or hovering within the disperse plume at some location downstream of the emission point. Hi-vol methods would be used for the collection of particulate species in the plume, while either grab sampling or concentration on XAD-2 resin would be used for gaseous constituents.

The acquisition of a sample directly from the larger unit is not considered possible because of the known variability of the flame and the tremendous radiant heat release that accompanies combustion. Remote sensing devices such as FTIR or laser methods are not sensitive or specific enough to obtain quantitative data.

A three-phased program was recommended, using the split stream approach with a focus on the evaluation of manual sampling.

A feasibility study report was supplied to EPA.

IV. Technical Assistance

One of the provisions of the contract was to provide a resource in the area of sampling and analysis of organic materials which would be available on a short-term quick response basis. During the course of the contract, considerable assistance was provided to a number of researchers from EPA and other government agencies, contract organizations and industry. The nature of the assistance ranged from telephone conversation, to limited chemical analysis of samples, to supplying resource materials such as reports, reference chemicals and sampling media.

Some examples of specific activities on this directive are listed below:

- Review MITRE FBC Level 1 - Level 2 Procedures Manual.
- Review phenol-from-cumene-process sampling test plan.
- Review the TRW Level 1 sampling and analysis report from the study at the KVB facility.
- Analyze an XAD-2 sample obtained from the Exxon FBC test.
- Consult with Radian Corporation on problems related to sampling of refinery fugitive emissions.
- Assist Acurex in selection of materials for use as an inert surface in SASS train.
- Review RTI Level 1 Environmental Assessment Performance Evaluation draft report.
- Revise MEG/Level 1 charts to reflect modification in Level 1 procedures.

- Review Monsanto dry bottom boiler test plan.

- Comment on incinerator PCB emission measurement procedures.

- Conduct collaborative test for nitrogen in shale oil to establish preferred procedure.

- Review TRW Conventional Combustion Environmental Assessment technicians manual.

- Provide assistance to IERL-RTP and TRW in the use of the SASS train for measurements of emissions in the Vulcanus test burns.

- Review York Research Corporation's coke oven quench tower test plans.

- Coordinate with IERL-RTP staff on problems in defining coal gasifier emission measurement approaches.

- Provide TRW with Level 2 organic analysis procedures.

- Provide coordination assistance, materials and staff time for the PMB booth at the APCA conference in Toronto organized by Southern Research Institute.

V. Reports and Published Papers

The following is a list of reports produced under this contract:

IERL-CRB Analysis Manual for Level 1 Environmental Assessment
J. C. Harris
Report No. ADL-79347-10-2 to Process Measurements Branch, IERL/RTP, February, 1977.

Instrumentation and Staffing Requirements for IERL-CRB Level 1 Environmental Assessment Laboratory
J. C. Harris
Report No. ADL-79347-10-3 to Process Measurements Branch, IERL/RTP, February, 1977.

Measurement of PCB in Sheepshead Minnows
A. B. Caragay and P. L. Levins
Report No. ADL-79347-12-2 to Process Measurements Branch, IERL/RTP, October, 1977.

Feasibility Study of a Breakthrough Indicator for the SASS Sorbent Module
C. F. Grain and D. B. Lindsay
Report to Process Measurements Branch, IERL/RTP, October, 1977.

Technical Manual for the Analysis of Fuels
L. N. Davidson, W. J. Lyman, D. Shooter and J. R. Valentine
Report EPA-600/7-77-143, December, 1977; NTIS PB-279 196/061.

Effect of Handling Procedures on Sample Quality
J. W. Adams, T. E. Doerfler and C. H. Summers
Report EPA-600/7-78-017, February, 1978; NTIS PB-279 910/4G1.

Characterization of Sorbent Resins for Use in Environmental Sampling
R. F. Gallant, J. W. King, P. L. Levins and J. F. Piecewicz
Report EPA-600/7-78-054, March, 1978, NTIS PB-284 347/2G1

EPA/IERL-RTP Interim Procedures for Level 2 Sampling and Analysis of Organic Materials
J. C. Harris and P. L. Levins
Report EPA-600/7-78-016, February, 1978; NTIS PB-279 212/5G1

Analytical Methods Recommendations for Organic Priority Pollutants for the Chemicals and Plastics Industry Category Verification Study
P. L. Levins and K. E. Thrun
Report No. ADL-79347-34 to the Process Measurements Branch, IERL/RT, April, 1978.

Sensitized Fluorescence for the Detection of Polycyclic Aromatic Hydrocarbons
E. M. Smith and P. L. Levins
Report EPA-600/7-78-182, September, 1978; NTIS PB-287 181/2GA

Support to Level 1 Environmental Assessment Study
D. B. Lindsay and L. H. Sadowski
Report No. ADL-73947-22 to Process Measurements Branch, IERL/RTP, December, 1978.

Ferroalloy Process Emissions Measurements
J. L. Rudloph, J. C. Harris, Z. A. Grosser and P. L. Levins
Report EPA-600/2-79-045, February, 1979; NTIS PB-293 171/5GA

Measurement of PCB Emissions from Combustion Sources
P.L. Levins, C. E. Rechsteiner and J. L. Stauffer
Report EPA-600/7-79-047, February, 1979. NTIS PB-293 360/4GA.

EPA/IERL-RTP Procedures for Level 2 Sampling and Analysis of Organic Materials
J. C. Harris, M. J. Hayes, P. L. Levins and D. B. Lindsay
Report EPA-600/7-79-033, February, 1979; NTIS PB-293 800/9GA

Gas Sample Storage
K. E. Thrun, J. C. Harris and K. Beltis
Report EPA-600/7-79-095, April, 1970; NTIS PB-298 350/0GA

Measurement of Polycyclic Organic Matter for Environmental Assessment
P. L. Levins, C. E. Rechsteiner and J. L. Stauffer
Report EPA-600/7-79-191, August, 1979; NTIS PB80-111966

Further Characterization of Sorbents for Environmental Sampling
J. F. Piecewicz, J. C. Harris and P. L. Levins
Report EPA-600/7-79-216, September, 1979; NTIS PB80-118763

Flare Sampling - A Feasibility Study
J. W. Adams
Report No. ADL-79347-23-1 to Process Measurements Branch, IERL/RTP, 1979.

Laboratory Evaluation of Level 1 Organic Analysis Procedures
J. C. Harris, Z. A. Grosser, P. L. Levins, D. J. Sorlin and C. H. Summers
Report No. ADL-79347-16 to Process Measurments Branch IERL/RTP, August, 1981.

Environmental Applications of Mass Spectrometry
P. L. Levins, J. E. Oberholtzer, C. E. Rechsteiner and J. L. Stauffer
Report No. ADL-79347-19 to Process Measurements Branch, IERL/RTP
August, 1981.

The following papers resulting from portions of the work carried out during the program have been published in technical journals and proceedings:

High Resolution Mass Spectrometry Matrix Analysis of Environmental Samples
J. L. Stauffer, P. L. Levins and J. E. Oberholtzer
Carcinogenesis, Vol. 3: Polynuclear Aromatic Hydrocarbons, Edited by P. W. Jones and R. I. Freudenthal, Raven Press, N.Y., 1978, pp. 89-95.

Quantitative Extraction of Polycyclic Aromatic Hydrocarbons and Other Hazardous Organic Species from Process Streams Using Macroreticular Resins
Z. A. Grosser, J. C. Harris and P. L. Levins in
Polynuclear Aromatic Hydrocarbons - Third International Symposium, Edited by P. W. Jones and P. Leber, Ann Arbor Science, 1979, pp. 67-79.

Sensitized Fluorescence Detection of PAH
E. M. Smith and P. L. Levins
Polynuclear Aromatic Hydrocarbons, Fourth Battelle Symposium, Battelle Press, Ohio, 1980, pp. 973-982.

A New Procedure for the Measurement of Polychlorinated Biphenyls (PCBs) in Combustion Sources
P. L. Levins, C. E. Rechsteiner and J. L. Stauffer
Journal American Institute of Chemical Engineers, 196, 330-337 (1980).